

Spectral Signatures of the Diffusional Anomaly in Water

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Analysis of power spectrum profiles for various tagged particle quantities in bulk SPC/E water is used to demonstrate that variations in mobility associated with the diffusional anomaly are mirrored in the exponent of the $1/f^\alpha$ region. Monitoring of $1/f^\alpha$ behaviour is shown to be a simple and direct method for linking phenomena on three distinctive length and time scales: the local molecular environment, hydrogen bond network reorganisations and the diffusivity. The results indicate that experimental studies of supercooled water to probe the density dependence of $1/f^\alpha$ spectral features, or equivalent stretched exponential behaviour in time-correlation functions, will be of interest.

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Supercooled water, unlike most liquids, shows an increase in molecular mobility with compression over certain ranges of temperature and pressure [1, 2, 3, 4]. Along an isotherm, this anomalous diffusional regime is bounded by densities corresponding to the diffusivity minimum and maximum [5, 6, 7, 8, 9, 10]. In this work, the diffusional anomaly is related to dynamical variations in the special structural features of water: a strong preference for local tetrahedral order and the presence of a fluctuating three-dimensional network of hydrogen bonds.

We use power spectral analysis to study temporal fluctuations in various observables. The power spectrum of a time-dependent mechanical quantity, $A(t)$, is defined as

$$S(f) = \left| \int_{t_{min}}^{t_{max}} (A(t) - \langle A \rangle) e^{2\pi i f t} dt \right|^2. \quad (1)$$

where $\langle A \rangle$ is the corresponding average over the system trajectory. In the case of water, power spectra associated with several quantities show a distinctive $1/f^\alpha$ type dependence on the frequency f [11, 12, 13, 14]. Such $1/f^\alpha$ or flicker noise is a generic feature of systems with multiple time scales [15] and, in this context, originates from hydrogen bond network rearrangements involving variable numbers of molecules. This study shows that the power spectrum profile associated with various quantities sensitive to the local molecular environment, particularly in the $1/f^\alpha$ regime, carries useful information on spatiotemporal correlations in the hydrogen bond network, including distinct signatures of the diffusional anomaly.

We have used the extended simple point charge (SPC/E) intermolecular potential for water [16] since the density, diffusional and compressibility anomalies of this model are well-characterised [7, 8, 9, 10]. Molecular dynamics (MD) simulations of bulk SPC/E water in the NVT ensemble were performed using the the DLPOLY software package [17, 18]. Simulation details are summarised in refs. [12, 14, 10].

Figure 1 shows the power spectra associated with different tagged particle quantities for bulk SPC/E water at 230K and 0.9 g cm^{-3} . The tagged molecule potential energy is the interaction energy of a given molecule with all other molecules in the system. The corresponding power spectrum, $S_u(f)$, shows a broad peak, centred around 500 cm^{-1} , due to the high-frequency, essentially single-molecule, librational modes. The $S_u(f)$ curve shows two regions of $1/f^\alpha$ -type behaviour: (i) the high frequency $60\text{-}298 \text{ cm}^{-1}$ range with $\alpha'_u = 1.56 \pm 0.02$ and (ii) the low frequency $1\text{-}40 \text{ cm}^{-1}$ region with $\alpha_u = 1.06 \pm 0.02$. The O-O stretch and O-O-O bending modes for bulk SPC/E water are known to occur at 200 and 50 cm^{-1} respectively [20] and therefore the high frequency $1/f^\alpha$ regime involves two or three-molecule hydrogen-bond network rearrangements. Since increasing delocalisation of vibrational modes results in lowering of the frequencies, the low frequency $1/f^\alpha$ regime must involve displacements of four to six molecules. Crossover to Markovian or white noise behaviour should occur below 1 cm^{-1} [13] which is a frequency regime not studied here. Also shown in Figure 1 is $S_{lib}(f)$ obtained from fluctuations in the librational kinetic energy, defined as the difference between the total and the centre-of-mass kinetic energies of a rigid molecule. $S_{lib}(f)$ shows no evidence of multiple time scale behaviour and the single prominent peak is again due to the librational modes.

The local structural order around a tagged oxygen atom is gauged by two order parameters, q_O and q_H . The degree of tetrahedrality of the four nearest hydrogen atoms surrounding a given oxygen atom i is measured by:

$$q_H = 1 - \frac{3}{8} \sum_{j=1}^3 \sum_{k=j+1}^4 (\cos \psi_{jk} + 1/3)^2 \quad (2)$$

where ψ_{jk} is the angle between the bond vectors \mathbf{r}_{ij} and \mathbf{r}_{ik} where j and k label the four nearest hydrogen atoms. The q_O order parameter is similarly defined using the positions of the four nearest oxygen atoms and has been

previously used to characterise orientational order in water [5]. The corresponding power spectra are labelled $S_O(f)$ and $S_H(f)$. The $S_H(f)$ curve shows a clear peak due to librational motion, unlike the $S_O(f)$ curve. Both $S_O(f)$ and $S_H(f)$ spectra show two $1/f^\alpha$ regimes with different exponents but in the case of $S_O(f)$, the higher frequency $1/f^\alpha$ regime stretches between 200-1000 cm^{-1} . The spectrum of fluctuations in the number of nearest oxygen atoms surrounding a tagged oxygen atom, $S_{NN}(f)$, is very similar to $S_O(f)$ [8].

The key features of the power spectral profiles are: (i) a broad librational peak (ii) a high-frequency $1/f^{\alpha'}$ regime above 50 cm^{-1} with exponent α' and (iii) a second, low-frequency multiple time scale regime in the range 1- 40 cm^{-1} with a different exponent α . A white noise region ($\alpha = 0$), seen at very low frequencies, becomes more pronounced at higher temperatures and/or higher densities, as discussed below. The librational peak is seen in $S_u(f)$, $S_H(f)$ and $S_{lib}(f)$ while the multiple time-scale regions are seen in all power spectra except $S_{lib}(f)$. At a given state point, the exact values of the exponents in the $1/f^\alpha$ regimes as well as the crossover frequencies depend on the specific quantities studied.

Figure 2 shows $S_u(f)$ at different densities for the 230K isotherm. At this temperature, SPC/E water has a diffusional minimum and maximum at $\rho_{min}=0.9 \text{ g cm}^{-3}$ and $\rho_{max}=1.1 \text{ g cm}^{-3}$ respectively [8, 9]. The librational region of the $S_u(f)$ curves changes qualitatively with density along this isotherm. It is most clearly demarcated at $\rho_{min}=0.9 \text{ g cm}^{-3}$ indicating that decoupling of librational modes from the hydrogen-bonded network rearrangements is maximal at this “ice” density. The librational peak moves to lower frequencies with increasing density and, for $\rho > \rho_{max}$, becomes a shoulder. We thus provide direct dynamical evidence that the anomalous diffusional regime, for which $dD/d\rho > 0$, is associated with increasing coupling of the librational modes with vibrations of the hydrogen-bonded network. This has been deduced in earlier work based on static structural distributions [8]. The density-dependent changes in the $1/f^\alpha$ regions of the power spectra are quantified by examining the associated exponents. Figure 3 shows that at 230K, the diffusivity, D , is strongly correlated with the low-frequency (1-40 cm^{-1}) exponent, α_u , and anticorrelated with the high frequency (60-298 cm^{-1}) exponent α'_u .

To understand the trends in the exponents of the $1/f^\alpha$ regions, it should be noted that power spectra generated using a uniform distribution of time scales between frequency limits λ_1 and λ_2 , show a $1/f$ regime ($\alpha \approx 1$) for $\lambda_1 < f < \lambda_2$, a white noise regime for $f \ll \lambda_1$ ($\alpha = 0$) and a Lorentzian tail ($\alpha \approx 2$) for $f \gg \lambda_2$ [15]. Thus α_u and α'_u will index the shapes of the multiple-time scale regime and the Lorentzian tail respectively. A separation of two decades in time scales between λ_1 and λ_2 is adequate for observing a $1/f^\alpha$ regime with α close to 1. At

ρ_{min} , the librational modes will be most effectively decoupled from the network vibrations, the range of available frequencies contributing to the $1/f$ regime will be the narrowest and the Lorentzian tail will be most pronounced. This is consistent with our observation that α'_u is maximum and α_u is ≈ 1 at ρ_{min} . In physical terms, it implies that at 230K and close to ρ_{min} , vibrational modes involving three or less molecules are significantly decoupled from more delocalised network re-organisations. We focus on the correlation with the diffusivity of the exponent α_u associated with the low-frequency, multiple scale region of the power spectrum. As librational modes become progressively more coupled to the network vibrations, high frequency components are introduced resulting in an increase in α_u with density in the anomalous regime between ρ_{min} and ρ_{max} . The decrease in α_u with increasing density for $\rho > \rho_{max}$ is due to increasing importance of steric effects which force the system to behave more like a simple liquid with $\alpha = 0$ [12].

The behaviour of the librational peak in $S_{lib}(f)$ and $S_H(f)$ at 230K is similar to that seen for $S_u(f)$ and the density dependence of the exponents in the $1/f^\alpha$ regions is shown in Figure 3. The α_H and α_O values are close to 1 in both cases. The density-dependent variations in these quantities, α_H and α_O , are smaller in magnitude than those of α_u though they show similar trends.

Increasing temperature or density results in coupling of librational modes to the network vibrations and at 300K, the librational band profile is virtually invariant with density. At 260K, two $1/f^\alpha$ regimes with different slopes can be seen with a low-frequency regime between 1-40 cm^{-1} and a high-frequency Lorentzian tail between 60-200 cm^{-1} . At 300K, only a single $1/f^\alpha$ regime can be seen between 4 and 200 cm^{-1} with a crossover to white noise behaviour between 0.1 and 0.5 cm^{-1} . Figure 4 illustrates very clearly the correlation between the density-dependent variations in the diffusivity and the exponent α_u . The attenuation of the diffusional anomaly with temperature and its disappearance at 300K are reflected in the behaviour of α_u .

We have also examined the $S_O(f)$ and $S_H(f)$ spectra at 260K and 300K. Compared to $S_u(f)$, the crossover to white noise behaviour occurs at higher frequencies for these quantities; for example, between 5 to 10 cm^{-1} , for $S_O(f)$ and $S_H(f)$ at 300K. This indicates that local tetrahedral order decorrelates faster than fluctuations in the tagged molecule potential energy.

This study establishes that the variations in mobility with pressure in the region of the diffusional anomaly are unambiguously mirrored in the exponent of the $1/f^\alpha$ region thus allowing one to monitor the dynamical effects of coupling the localised librational modes to the hydrogen-bonded network. The range of frequency over which $1/f^\alpha$ behaviour is observed, including the frequency of crossover to white noise, provides a quantitative assessment of the time and length scales over which correla-

tions in the network vanish. Moreover, $1/f^\alpha$ behaviour is not equally pronounced for all observables, due to differing sensitivities to processes operating on different time scales.

The significance of the present results derive from the clear connections that can be drawn between between three distinctive length and time scale features of bulk water: the local molecular environment, the hydrogen bond network reorganisations and the diffusivity which is a long-time averaged transport property. This approach provides a possible route for understanding the connection between structural order and the static and dynamic anomalies of water [5, 21] and can be extended to other hydrogen-bonded systems or networked liquids. Our work also suggests that it would be of interest to examine the connection between $1/f^\alpha$ behaviour and spatiotemporal heterogeneity in supercooled liquids since the distribution of length and time scales in the system is expected to widen as one approaches the kinetic glass transition. In the context of water, such a kinetic glass transition is predicted for SPC/E water around 190K at 1 g cm^{-3} [22, 26]; the experimental value is around 225K [2, 23]. Near this dynamical transition, water behaves in a very similar manner to the binary Lennard-Jones glass-formers with no apparent effect of the hydrogen bond network. Our $1/f^\alpha$ analysis shows that by 230K, two and three-molecule vibrational modes are shifted into the Lorentzian tail, indicating that these vibrational frequencies are progressively decoupled from overall network reorganisations. As the temperature is reduced further, one would expect the multiple time-scale regime to shift to lower frequencies and involve larger clusters; the dynamics of these larger clusters may be insensitive to directional bonding and local tetrahedral order.

Our results have interesting implications for experimental work on water and aqueous solutions, specially in the context of hydration of biomolecules [24, 25]. We show that different observables will have different degrees of sensitivity to the underlying multiple time-scale dynamics of the hydrogen-bonded network and therefore the choice of spectroscopic technique is likely to be significant. For example, the behaviour of high-frequency librational modes as a function of density can be studied by ultrafast spectroscopy [29]. Experimental evidence for $1/f^\alpha$ behaviour, or the equivalent stretched exponential behaviour of time-correlation functions, exists from inelastic neutron scattering, Raman and, most recently, optical Kerr effect measurements [22, 23, 27, 28]. The pressure or density dependence of the exponents has not been examined so far and our work indicates that these will be of considerable interest [23].

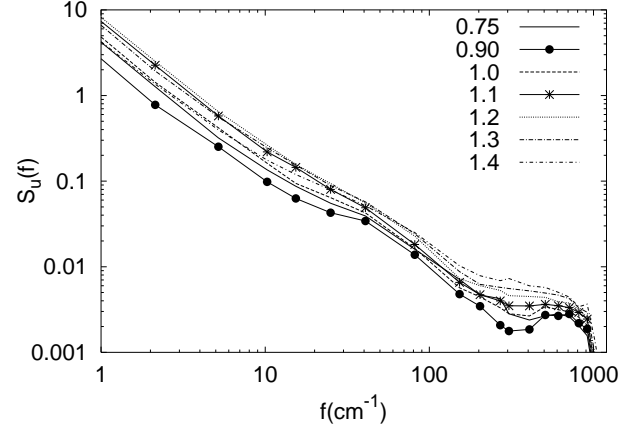
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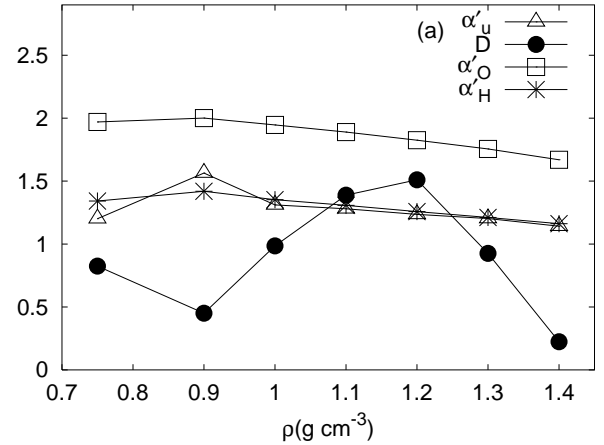
Figure Captions

1. Power spectra associated with temporal fluctuations in different tagged particle quantities at 230K and 0.9 g cm^{-3} . The different curves represent $S_u(f)$ (thick solid line), $S_{lib}(f)$ (solid line), $S_{NN}(f)$ (dot-dashed line), $S_O(f)$ (dotted line) and $S_H(f)$ (dashed line). Arrows show the O-O stretch (200 cm^{-1}), O-O-O bend (50 cm^{-1}) and the librational region ($400\text{-}1000 \text{ cm}^{-1}$) [20]. Systems at a density of 0.75 g cm^{-3} are likely to be inhomogeneous [8].
2. Power spectra, $S_u(f)$, at different densities (in g cm^{-3}) along the 230K isotherm.
3. Behaviour of the exponent associated with the $1/f^\alpha$ regimes as a function of density at 230K. Part (a) shows the exponents associated with the high-frequency $1/f^\alpha$ regime with α'_u , α'_H and α'_O evaluated over the frequency ranges $60\text{-}298 \text{ cm}^{-1}$, $90\text{-}298 \text{ cm}^{-1}$ and $200\text{-}1000 \text{ cm}^{-1}$ respectively. Part (b) shows the exponents associated with the low-frequency $1/f^\alpha$ regime with α_u , α_H and α_O evaluated over the the $1\text{-}40 \text{ cm}^{-1}$ range. Also shown is the diffusivity, D , in units of $2 \times 10^{-6} \text{ cm}^2/\text{s}$.
4. Dependence on density, ρ , of (a) the diffusivity, D , and (b) the exponent α_u along isotherms at 230K, 260K and 300K. The exponent α_u is evaluated using the low-frequency $1/f^\alpha$ regime from $1\text{-}40 \text{ cm}^{-1}$ at 230K to 280K and over the frequency range $4\text{-}200 \text{ cm}^{-1}$ at 300K.

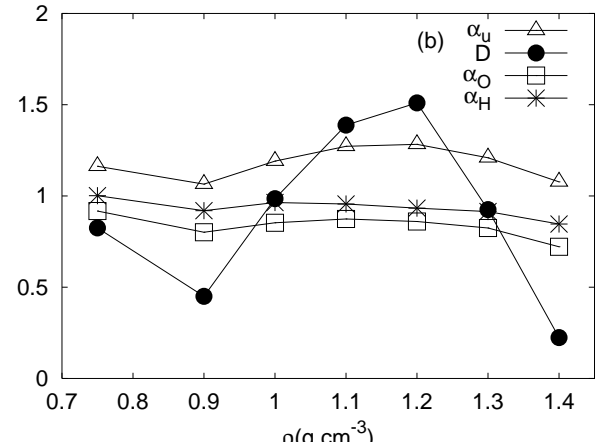
chakravarty-fig2



chakravarty-fig3a



chakravarty-fig3b



chakravarty-fig1

